

# TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER

Mo-7058/LeA 34,016

U.S. APPLICATION NO. (If known, see 37 CFR 1.5

To Be Assigned **10/089709**

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/09372

26 September 2000 (26.09.00)

08 October 1999 (8.10.99)

TITLE OF INVENTION

THERMOFORMABLE POLYAMIDES

APPLICANT(S) FOR DO/EO/US POPHUSEN, Dirk; JOACHIMI, Detlev and ROHNER, Jorgen

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☒ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Form PTO 1449 w/references

To Be Assigned **1089709**

PCT/EP00/09372

Mo-7058/LeA 34,016

21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1)-(5)):**

Neither international preliminary examination fee (37 CFR 1.482)  
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
and International Search Report not prepared by the EPO or JPO ..... **\$1040.00**

International preliminary examination fee (37 CFR 1.482) not paid to  
USPTO but International Search Report prepared by the EPO or JPO ..... **\$890.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO  
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... **\$740.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
and all claims satisfied provisions of PCT Article 33(1)-(4) ..... **\$100.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS PTO USE ONLY**

\$ 890.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	14 - 20 =	0	x \$18.00	\$ 0.00
Independent claims	3 - 3 =	0	x \$84.00	\$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$280.00 \$ 0.00
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$ 890.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				+ \$ 0.00
<b>SUBTOTAL =</b>				\$ 890.00
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ 0.00
<b>TOTAL NATIONAL FEE =</b>				\$ 890.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property +				\$ 40.00
<b>TOTAL FEES ENCLOSED =</b>				\$ 930.00
				Amount to be refunded: \$
				charged: \$

a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 930.00 to cover the above fees.  
A duplicate copy of this sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848 A duplicate copy of this sheet is enclosed.d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

**00157**

PATENT TRADEMARK OFFICE

SIGNATURE

Aron Preis

NAME

29,426

REGISTRATION NUMBER

10/089709

JG13 Rec'd PGT/PTO 01 APR 2002

PATENT APPLICATION

Mo-7058

LeA 34,016

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF )  
DIRK POPHUSEN ET AL )  
SERIAL NUMBER: TO BE ASSIGNED )  
FILED: HEREWITH )  
TITLE: THERMOFORMABLE POLYAMIDES )

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to the examination of the instant patent application kindly amend the enclosed translation thereof as follows:

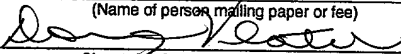
"Express Mail" mailing label number ET671453164US

Date of Deposit April 1, 2002

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)

  
Signature of person mailing paper or fee)

10089709-040102

IN THE ABSTRACT:

Please add an abstract page reading as follows:

--THERMOFORMABLE POLYAMIDES

ABSTRACT OF THE DISCLOSURE

A reinforced polyamide molding composition is disclosed. Characterized in that its viscosity at a shear velocity of  $10 \text{ s}^{-1}$  is greater than 1000 Pas and at a shear velocity of  $1000 \text{ s}^{-1}$  is less than 300 Pas, at processing temperatures of 40 to 80°C above its melting point, the composition is particularly suitable for thermoforming applications.--

IN THE CLAIMS:

Cancel Claims 3, 4, 5 and 6.

Add the following:

- 7. A method of using the composition of Claim 1 comprising preparing an article by thermoforming.
8. A method of using the composition of Claim 2 comprising preparing an article by thermoforming.
9. A method of preparing an article comprising thermoforming a composition comprising
- A) 98 to 41 parts by weight of a thermoplastic partially crystalline polyamide, and
  - B) 2 to 50 parts by weight of reinforcing materials, and
  - C) 0.1 to 4 parts by weight of branching additives and/or additives raising the molecular weight and
  - D) 0 to 5 parts by weight of further additives,
- the sum of the parts by weight of A, B, C, D totalling 100.

10. The method of Claim 9 wherein C is a diepoxide.
11. A method of preparing an article comprising thermoforming a composition comprising
- A) 67 to 85 parts by weight of a thermoplastic partially crystalline polyamide and
  - B) 15 to 30 parts by weight of reinforcing materials, and
  - C) 0.2 to 1 part by weight of branching additives and/or additives raising the molecular weight,
  - D) 0.1 to 2 parts by weight of further additives,
- the sum of the parts by weight of A, B, C and D totaling 100.
12. The method of Claim 11 wherein C is a diepoxide.
13. A molded article obtained by the method of Claim 7.
14. A molded article obtained by the method of Claim 8.
15. A molded article obtained by the method of Claim 9.
16. A molded article obtained by the method of Claim 10.
17. A molded article obtained by the method of Claim 11.
18. A molded article obtained by the method of Claim 12.--

REMARKS

The present amendment seeks to place the application in better conformance with U.S. practice. A new Abstract page is included herewith.

Entry of the amendment is requested.

Respectfully submitted,

By



Aron Preis  
Attorney for Applicants  
Reg. No. 29,426

Bayer Corporation  
100 Bayer Road  
Pittsburgh, Pennsylvania 15205-9741  
(412) 777-8343  
FACSIMILE PHONE NUMBER:  
(412) 777-8363

s:/sr/ap0283

**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE ABSTRACT:**

Please add an abstract page reading as follows:

**--THERMOFORMABLE POLYAMIDES**

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A reinforced polyamide molding composition is disclosed. Characterized in that its viscosity at a shear velocity of  $10 \text{ s}^{-1}$  is greater than 1000 Pas and at a shear velocity of  $1000 \text{ s}^{-1}$  is less than 300 Pas, at processing temperatures of 40 to 80°C above its melting point, the composition is particularly suitable for thermoforming applications.--

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  - G) 0.1 to 4 parts by weight of branching additives and/or additives raising the molecular weight and

H) 0 to 5 parts by weight of further additives,  
the sum of the parts by weight of A, B, C, D totalling 100.

10. The method of Claim 9 wherein C is a diepoxide.
11. A method of preparing an article comprising thermoforming a composition comprising
  - A) 67 to 85 parts by weight of a thermoplastic partially crystalline polyamide and
  - B) 15 to 30 parts by weight of reinforcing materials, and
  - C) 0.2 to 1 part by weight of branching additives and/or additives raising the molecular weight,
  - D) 0.1 to 2 parts by weight of further additives,the sum of the parts by weight of A, B, C and D totaling 100.
12. The method of Claim 11 wherein C is a diepoxide.
13. A molded article obtained by the method of Claim 7.
14. A molded article obtained by the method of Claim 8.1
15. A molded article obtained by the method of Claim 9.
16. A molded article obtained by the method of Claim 10.
17. A molded article obtained by the method of Claim 11.
18. A molded article obtained by the method of Claim 12.--



THERMOFORMABLE POLYAMIDESABSTRACT OF THE DISCLOSURE

A reinforced polyamide molding composition is disclosed. Characterized in that its viscosity at a shear velocity of  $10 \text{ s}^{-1}$  is greater than 1000 Pas and at a shear velocity of  $1000 \text{ s}^{-1}$  is less than 300 Pas, at processing temperatures of 40 to  $80^\circ\text{C}$  above its melting point, the composition is particularly suitable for thermoforming applications.

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Thermoformable Polyamides

The present invention relates to glass fibre-reinforced polyamides and the use of the latter for thermoforming.

5

The thermoforming of thermoplastic semi-finished products has become increasingly important in recent years. Not least, the possibility of being able to develop prototypes quickly offers advantages compared to the more expensive rival processes such as injection moulding processes. Constantly improved thermoplastic materials enable the output to be increased with modern machinery and tools, combined at the same time with improved precision of the mouldings (Kunststoff Handbuch 3 / 4 "Polyamide", Hanser Verlag, Munich, Vienna).

10

Polyamides, and in the present context in particular reinforced polyamides from the group comprising partially crystalline thermoplastic materials, were hitherto largely excluded from thermoforming applications (Thermoformen in der Praxis, p. 45 ff, Hanser Verlag, Munich, Vienna). The very narrow processing window of this class of materials, which allowed forming to be carried out only just below the crystalline melting point, and the insufficient melt stabilities of these polymeric materials as a result of the low melt viscosities, enabled semi-finished products (sheets) produced therefrom to be formed only into very flat mouldings with low stretch/draw ratios and reduced shaping sharpness.

15

20

The thermoforming of films, which is often referred to as deep drawing, is known for polyamide films (single-layer, multi-layer, co-extruded or laminated) (Verpacken mit Kunststoffen, Hanser Verlag, Munich, Vienna). The person skilled in the art refers to films having a thickness of less than 1500 µm as suitable for deep drawing applications (Thermoformen, Hanser Verlag, Munich, Vienna, 1999).

25

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Donna J. Veatch

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The object therefore existed of providing a reinforced polyamide from which thermoplastic semi-finished products can be then produced having a material thickness of greater than 1.5 mm, from which in turn mouldings can be produced by thermoforming having a high degree of forming and a good shaping sharpness.

5

It has now surprisingly been found that polymeric materials from the class of materials of pseudoplastic reinforced polyamides, such as are described for example in EP-A 0 685 528, with a viscosity behaviour according to the invention, are extremely suitable for thermoforming. Degrees of forming can be obtained that are significantly better than those achievable with hitherto known materials. The materials also have a large forming temperature range.

10

These moulding compositions are characterised by their clearly defined pseudoplastic behaviour compared to standard polyamides. In other words, these moulding compositions have a significantly higher viscosity at low shear velocities compared to standard polyamides and comparably high viscosities at high shear velocities. This pseudoviscosity is achieved via an increased degree of branching of these polyamides. This can be achieved on the one hand in the primary condensation in a so-called VC tube, or also in a subsequent compounding.

15

20

The reinforcement of polyamides is carried out in a known manner by incorporating for example glass fibres or mineral fillers in the polyamide melt, for example from an extruder.

25

The present invention accordingly provides reinforced polyamide moulding compositions whose viscosity at a shear velocity of  $10 \text{ s}^{-1}$  is greater than 1000 Pas and at a shear velocity of  $1000 \text{ s}^{-1}$  is less than 300 Pas, at a processing temperature of 40 to  $80^\circ\text{C}$  above the melting point of the relevant moulding composition.

Reinforced polyamide moulding compositions are preferred whose viscosity at a shear velocity of  $10 \text{ s}^{-1}$  is greater than 1500 Pas and at a shear velocity of  $1000 \text{ s}^{-1}$  is less than 280 Pas, at a processing temperature of  $40 - 80^\circ\text{C}$  above the melting point of the relevant moulding composition

5

The invention also provides for the use of these moulding compositions according to the invention for thermoforming.

It is preferred to use moulding compositions containing:

10

- A) 98 to 41 parts by weight of thermoplastic partially crystalline polyamide and
- B) 2 to 50 parts by weight of reinforcing materials
- C) 0.1 to 4 parts by weight of branching additives and/or additives raising the molecular weight, for example diepoxide
- D) 0 to 5 parts by weight of further additives, for example processing additives for thermoforming, colouring agents, carbon black.

15

the sum of the parts by weight of A, B, C and D totalling 100,

20

for thermoforming.

It is particularly preferred to use moulding compositions containing

25

- A) 67 to 85 parts by weight of thermoplastic partially crystalline polyamide and
- B) 15 to 30 parts by weight of reinforcing materials
- C) 0.2 to 1 part by weight of branching additives and/or additives raising the molecular weight, for example diepoxide

- 4 -

D) 0.1 to 2 parts by weight of further additives, for example processing additives for thermoforming, colouring agents, carbon black,

the sum of the parts by weight of A, B, C and D totalling 100,

5

for thermoforming.

The application also provides thermoformed moulded bodies obtainable from the  
aforedescribed used moulding compositions.

10

Partially crystalline polyamides (PA), preferably PA 6, PA 66, PA 46, PA 610, PA 6/6T or partially crystalline copolyamides or mixtures based on these components are suitable as thermoplastic polyamide A).

15

The class of substances comprising polyamides is described in Kunststoff Handbuch 3 / 4 "Polyamide", Hanser Verlag, Munich, Vienna. This relates in particular to the production of the base resins (Chapter 2.1), as well as their modification (Chapter 2.3) and their reinforcement (Chapter 2.4).

20

A large number of procedures are known for producing polyamides, different monomer building blocks, various chain regulators for achieving a desired molecular weight or also monomers with reactive groups for subsequently intended post-treatment procedures being used depending on the desired end product.

25

The technically relevant processes for producing polyamides take place without exception via polycondensation in the melt. The hydrolytic polymerisation of lactams is also understood as polycondensation in this context.

30

Preferred polyamides for the moulding compositions according to the invention are partially crystalline polyamides that can be produced starting from diamines and

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dicarboxylic acids and/or lactams having at least five ring members or corresponding amino acids.

Suitable starting products are preferably aliphatic dicarboxylic acids such as adipic acid, 2,2,4- and 2,4,4-trimethyladipic acid, azelaic acid, sebacic acid, aliphatic diamines such as hexamethylene diamine, 2,2,4- and 2,4,4-trimethylhexamethylene diamine, the isomeric diaminodicyclohexylmethanes, diaminodicyclohexylpropanes, bis-aminomethylcyclohexane, aminocarboxylic acids such as aminocaproic acid and/or the corresponding lactams. Copolyamides of several of the aforementioned monomers are included.

Particularly preferred are caprolactams, and most particularly preferred is  $\epsilon$ -caprolactam.

Polyamide 6 and/or polyamide 6,6 are particularly preferably used. Polyamide 6 is most particularly preferably used.

The polyamides produced according to the invention may also be used mixed with other polyamides and/or further polymers.

Commercially available glass fibres, carbon fibres, mineral fibres, fillers with or without surface treatment, etc., for polyamides, are used individually or in mixtures as reinforcing materials B). Preferred fibre-shaped or particle-shaped fillers and reinforcing materials are glass fibres, glass spheres, glass fabrics, glass mats, aramide fibres, carbon fibres, potassium titanate fibres, natural fibres, amorphous silicic acid, magnesium carbonate, barium sulfate, feldspar, mica, silicates, quartz, kaolin, talcum, titanium dioxide, wollastonite, i.a., which may also be surface treated. Particularly preferred reinforcing materials are commercially available glass fibres. The glass fibres, which generally have a fibre diameter of between 8 and 18  $\mu\text{m}$ , may be added as endless fibres or as cut or ground glass fibres, in which

connection the fibres may be treated with a suitable sizing system and a coupling agent or coupling agent system, for example based on silane.

As branching additives C) for the moulding compositions according to the invention, there are used for example commercially available diepoxides based on diglycidyl ether (bisphenol A and epichlorohydrin), based on aminoepoxide resins (aniline and epichlorohydrin), based on diglycidyl esters (cycloaliphatic dicarboxylic acids and epichlorohydrin) individually or in mixtures, as well as, preferably, diepoxides based on 2,2-bis[p-hydroxyphenyl]-propane diglycidyl ether, bis-[N-methyl-N-2,3-epoxypropylaminophenyl]-methane.

As component D there may be used conventional additives such as agents against thermal decomposition, agents against thermal crosslinking, agents against damage by UV light, plasticisers, lubricants and mould release agents, nucleating agents, stabilisers, as well as dyes and pigments.

Examples of oxidation inhibitors and thermal stabilisers are sterically hindered phenols and/or phosphites, hydroquinones, aromatic secondary amines such as diphenylamines, various substituted members of these groups and their mixtures in concentrations of up to 1 wt.% referred to the weight of the thermoplastic moulding compositions.

As UV stabilisers, which are generally used in amounts of up to 2 wt.% referred to the moulding composition, there may be mentioned various substituted resorcinols, salicylates, benzotriazoles and benzophenones.

Inorganic pigments such as titanium dioxide, ultramarine blue, iron oxide and carbon black, and furthermore organic pigments such as phthalocyanines, quinacridones, perylenes as well as dyes such as anthraquinones may be added as colouring agents, together with other colouring agents.

As nucleating agents there may for example be used sodium phenyl phosphinate, aluminium oxide, silicon dioxide as well as, preferably, talcum.

5 Lubricants and mould release agents, which are conventionally used in amounts of up to 1 wt.%, are preferably ester waxes, pentaerythritol stearate (PETS), long-chain fatty acids (for example stearic acid or behenic acid), their salts (e.g. Ca or Zn stearate) as well as amide derivatives (e.g. ethylene bis-stearylamine) and also low molecular weight polyethylene or polypropylene waxes.

10

Thermoforming (heat forming) is understood in this patent application to denote a production process in which a thermoplastic film or sheet is heated up to the softening point, is formed at low pressure in a tool, is cooled and then post-treated. All thermoplastic materials that can be produced as films or sheets are in principle  
15 also thermoformable, with the proviso that the temperature does not exceed the thermal stability of the material. The inherent strength should be sufficient to prevent an excessive sag resulting in tearing of the film or sheet. The thickness range of freely thermoformable semi-finished products extends from 0.1 mm thick films up to 10 mm thick sheets (Kunststoff Handbuch 3 / 4 "Polyamide" Hanser  
20 Verlag, Munich, Vienna. p. 459, 460.

In thermoforming only one side of the heated semi-finished product comes into contact with the forming tool. The surface contours of the forming tool are accurately reproduced on the application side of the semi-finished product. The  
25 contour and also the dimensions on the other side of the formed part are governed by the resulting wall thickness of the thermoformed part. In principle a distinction is made between positive and negative forming depending on whether the inside or outside of the formed part is brought into contact with the forming tool. The forming accuracy on the internal contour (positive forming) or on the external  
30 contour (negative forming) of the moulding is determined accordingly.



The basic advantages of thermoforming are inexpensive thermoforming tools, cheaper thermoforming machinery, and the possibility of also being able to process multi-layer materials, foamed substances and pre-printed semi-finished products

5 ("Thermoformen in der Praxis", Schwarzmann, P., Hanser Verlag, Munich, Vienna, 1997).

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### Examples and Comparison Examples

The following features were adopted for the evaluation of the quality of the thermoformed articles:

5

- **Degree of forming and stretch/draw ratio**

The degree of forming is the ratio of the maximum drawing depth H to the width B or the diameter D of the forming surface (clear width of the clamping frame surface).

10

The stretch/draw ratio is the ratio of the surface of the moulding before trimming (without the clamping frame), to the moulding surface.

- **Thermoformability**

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The forming behaviour is evaluated. The sheet-like semi-finished product should exhibit a sufficient strength with low sag in the clamping frame during the heating phase and should easily be able to be shaped by the tool without producing melt overhangs and folds. The evaluation is made according to a points scale (1 = very good, 6 = unsatisfactory).

20

- **Wall thickness distribution**

25

The wall thickness of the individual stages of the mouldings produced with the multi-stage die is measured and the uniformity is evaluated. The arithmetic mean of the individual values of the stages, as well as the maximum deviation from the mean value referred to the mean value is determined for this purpose. The evaluation is made according to a points scale (1 = very good, 6 = unsatisfactory).

- **Shaping sharpness**

The term shaping sharpness is understood to mean the accuracy of reproduction of the contours of the thermoforming tool on the moulding. Small radii and surface structures on the application side to the tool are mainly adopted as criteria.

The shaping in the corner region was evaluated. The evaluation was made on the basis of a points scale (1 = very good shaping, 6 = unsatisfactory shaping).

Mouldings are produced from the material used according to the invention and from comparison material, and are compared and evaluated.

The following products are used:

PA 6: Durethan® B 31 from Bayer AG (relative solution viscosity: 3, measured in 1% m-cresol solution at 25°C)

Diepoxide: Rütapox 0162 from Bakelite AG (diepoxide based on bisphenol A and epichlorohydrin)

Glass fibres: CS 7923 from Bayer AG, Leverkusen, Germany

Additives: Nucleating agent (micronised talcum)

Heat stabiliser (CuJ/alkali halides)

Carbon black

#### Example B1

The components listed hereinafter were compounded in a twin-screw extruder (ZSK) from Werner & Pfleiderer (100 min<sup>-1</sup>; 10 kg/h) at 265°C, extruded in a water bath, and granulated. The diepoxide was metered from a liquid metering pump into the feed section of the extruder.

- 11 -

	<u>Description</u>	<u>Wt. %</u>
	PA 6	84%
	Glass fibres	15%
	Diepoxide	0.5%
5	Additives	0.5%

Comparison Example VB1

10 The components listed hereinafter were compounded in a twin-screw extruder from Werner & Pfleiderer (100 min<sup>-1</sup>; 10 kg/h) at 265°C, extruded in a water bath and granulated.

	<u>Description</u>	<u>Wt. %</u>
	PA 6	84.5%
15	Glass fibres	15%
	Additives	0.5%

Example B2

20 The components listed hereinafter were compounded in a twin-screw extruder from Werner & Pfleiderer (100 min<sup>-1</sup>; 10 kg/h) at 265°C, extruded in a water bath and granulated. The diepoxide was metered from a liquid metering pump into the feed section of the extruder.

	<u>Description</u>	<u>Wt. %</u>
25	PA 6	68.8%
	Glass fibres	30%
	Diepoxide	0.5%
	Carbon black	0.2%
30	Additives	0.5%

Comparison Example VB2

The components listed hereinafter were compounded in a twin-screw extruder from Werner & Pfleiderer (100 min<sup>-1</sup>; 10 kg/h) at 265°C, extruded in a water bath and granulated.

<u>Description</u>	<u>Wt. %</u>
PA 6	69.3%
Glass fibres	30%
Carbon black	0.2%
Additives	0.5%

The granules obtained were in each case dried for 4 hours at ca. 70°C in a vacuum drying cabinet.

The melt viscosities of the produced polymers were then measured in a capillary rheometer (DIN 54811-B) at various shear viscosities and temperatures. The measured values were in each case converted into the true shear velocities and true viscosities. The following table shows a comparison for three shear velocities at a melt temperature of  $\theta_m = 280^\circ\text{C}$  (melting point of PA ca. 220°C).

Table 1

Viscosity at $\theta_m = 280^\circ\text{C}$ in Pas	B1	VB1	B2	VB2
Viscosity at shear velocity 10 s <sup>-1</sup>	2100	340	2000	600
Viscosity at shear velocity 1000 s <sup>-1</sup>	250	130	220	290

The necessary sheet-like semi-finished products were made using the granules produced by way of example, in an extrusion unit. The polymer granules were extruded via an extruder through a slit die and withdrawn through a polishing stack

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and calibrated. Sheets 3 mm thick and 800 mm wide were thus produced in this way, and were cut into ca. 1100 mm long sections.

5 The sheet-like semi-finished products were thermoformed in a thermoforming unit from Illig (Type Illig UA 100 Thermoform-Anlage). A rectangular multi-stage die was used as thermoforming tool (TW), which enables different material behaviours to be evaluated easily. The multi-stage die that was used allows different drawing depths to be adjusted, by varying the number of the stages (3 stages/5 stages/7 stages). The individual stage height is in each case 30 mm.

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The thermoformability, the wall thicknesses and the shaping sharpness were compared in each case for the adjusted stretch/draw ratios listed in the following table.

15 Table 2

Tool Designation	No. of Stages	Drawing Depth	Degree of Forming	Stretch/Draw Ratio
TW7	7	210 mm	82%	241%
TW5	5	150 mm	59%	192%
TW3	3	90 mm	35%	153%

The results obtained with the mouldings produced with the sheets extruded by way of example are reproduced in the following Table.

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Table 3

	B1	VB1	B2	VB2
Thermoformability with TW 3	1	3	1	3
Wall thickness distribution with TW 3	1	4	1	3
Shaping sharpness with TW 3	2	4	1	3
Remarks		Tears		Tears
Thermoformability with TW 5	1	5	1	5
Wall thickness distribution with TW 5	2	4	1	5
Shaping sharpness with TW 5		4	1	4
Remarks		Large holes		Large holes
Thermoformability with TW 7	2	6	1	6
Wall thickness distribution with TW 7	2	6	1	5
Shaping sharpness with TW 7	2	5	1	6
Remarks		Thermoforming not possible		Thermoforming not possible

5 The quality was evaluated in this case using a points scale (1 = very good, 6 = unsatisfactory), see Description.

From Table 3 it can be seen that the examples according to the invention exhibit significantly better thermoformability, wall thickness distribution and shaping sharpness.

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Thermoforming was carried out at adjusted surface temperatures of  $T = 235^{\circ}\text{C}$  to  $254^{\circ}\text{C}$  for B1 and B2, and also as  $T = 225^{\circ}\text{C}$  up to  $230^{\circ}\text{C}$  for VB1 and VB2.

**Patent Claims**

1. Reinforced polyamide moulding compositions whose viscosity at a shear velocity of  $10 \text{ s}^{-1}$  is greater than 1000 Pas and at a shear velocity of  $1000 \text{ s}^{-1}$  is less than 300 Pas, at a processing temperature of 40 to  $80^\circ\text{C}$  above the melting point of the relevant moulding composition.
2. Reinforced polyamide moulding compositions whose viscosity at a shear velocity of  $10 \text{ s}^{-1}$  is greater than 1500 Pas and at a shear velocity of  $1000 \text{ s}^{-1}$  is less than 280 Pas, at a processing temperature of 40 to  $80^\circ\text{C}$  above the melting point of the relevant moulding composition.
3. Use of the moulding compositions according to claim 1 and/or 2 for thermoforming.
4. Use of reinforced moulding compositions containing
- A) 98 to 41 parts by weight of thermoplastic partially crystalline polyamide and
  - B) 2 to 50 parts by weight of reinforcing materials
  - C) 0.1 to 4 parts by weight of branching additives and/or additives raising the molecular weight, e.g. diepoxide
  - D) 0 to 5 parts by weight of further additives, e.g. processing additives for thermoforming,

the sum of the parts by weight of A, B, C, D totalling 100,

for thermoforming.



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6. Mouldings obtainable according to one or more of the preceding claims.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
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(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von US): BAYER AKTIENGESELLSCHAFT [DE/DE]; 51368 Leverkusen (DE).

(72) Erfinder; und

(75) Erfinder/Anmelder (nur für US): POPHUSEN, Dirk [DE/DE]; Carl-Rumpff-Str. 5, 51373 Leverkusen (DE). JOACHIMI, Detlev [DE/DE]; Scheiblerstr. 103, 47800 Krefeld (DE). RÖHNER, Jürgen [DE/DE]; Brambachstr. 86, 51069 Köln (DE).

(81) Bestimmungsstaaten (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

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**Veröffentlicht:**

— Mit internationalem Recherchenbericht.

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: THERMOFORMABLE POLYAMIDES

(54) Bezeichnung: THERMOFORMBARE POLYAMIDE

(57) Abstract: The invention relates to glass-fiber reinforced polyamides and to the use thereof for thermoforming.

(57) Zusammenfassung: Die Erfindung betrifft glasfaserverstärkte Polyamide und die Verwendung dieser zum Thermoformen.

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**COMBINED DECLARATION AND POWER OF ATTORNEY**

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

**THERMOFORMABLE POLYAMIDES**

the specification of which is attached hereto,

or was filed on **September 26, 2000**

as a PCT Application Serial No. **PCT/EP00/09372**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

**199 48 850.9**  
(Number)

**Germany**  
(Country)

**October 8, 1999**  
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Le A 34 016-US

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JK

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

JOSEPH C. GIL, Patent Office Registration Number 26,602; ARON PREIS, Patent Office Registration Number 29,426; LYNDANNE M. WHALEN, Patent Office Registration Number 29,457; THOMAS W. ROY, Patent Office Registration Number 29,582; RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619; GODFRIED R. AKORLI, Patent Office Registration Number 28,779; N. DENISE BROWN, Patent Office Registration Number 36,097; NOLAND J. CHEUNG, Patent Office Registration Number 39,138; DIDERICO VAN EYL, Patent Office Registration Number 38,641; CAROLYN M. SLOANE, Patent Office Registration Number 44,339; JAMES R. FRANKS, Patent Office Registration Number 42,552; JACKIE ANN ZURCHER, Patent Office Registration Number 42,251; RAYMOND J. HARMUTH, Patent Office Registration Number 33,896; JOHN E. WROZINSKI, JR., Patent Office Registration Number 46,179; JENNIFER R. SENG, Patent Office Registration Number 48,851, all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Send Correspondence To:  
Patent Department  
Bayer Corporation  
100 Bayer Road  
Pittsburgh, Pennsylvania 15205-9741

Direct Telephone Calls To:

(412) 777-2349

FULL NAME OF SOLE OR FIRST INVENTOR Dirk Pophusen		INVENTOR'S SIGNATURE <i>[Signature]</i>	DATE 2002-02-21
RESIDENCE D 51373 Leverkusen, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS c/o BAYER AKTIENGESELLSCHAFT, D 51368 Leverkusen, Germany			
FULL NAME OF SECOND INVENTOR Detlev Joachimi		INVENTOR'S SIGNATURE <i>[Signature]</i>	DATE 2002-02-19
RESIDENCE D 47800 Krefeld, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS c/o BAYER AKTIENGESELLSCHAFT, D 51368 Leverkusen, Germany			
FULL NAME OF THIRD INVENTOR Jürgen Röhner		INVENTOR'S SIGNATURE <i>[Signature]</i>	DATE 26.02.02
RESIDENCE D 51069 Köln, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS c/o BAYER AKTIENGESELLSCHAFT, D 51368 Leverkusen, Germany			
FULL NAME OF FOURTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FIFTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SIXTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			